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TECHNICAL REPORT

THE REACTION OF ATOMIC OXYGEN WITH ACETYLENE (II)
CHEMI-IONIZATION AND CHEMILUMINESCENCE

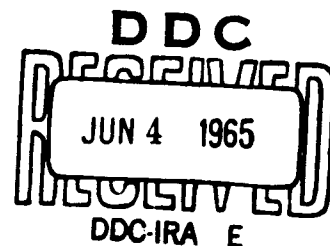
C. A. Arrington, W. Brennen, G. P. Glass,
J. V. Michael and H. Niki

Submitted to
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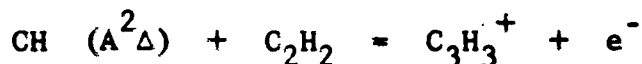
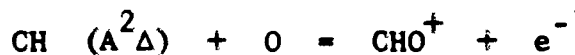
THE REACTION OF ATOMIC OXYGEN WITH ACETYLENE (II)
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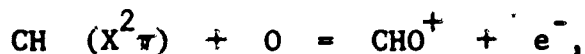
ABSTRACT

The chemiluminescence and chemi-ionization resulting from the room temperature reaction of atomic oxygen with acetylene have been investigated. The absolute intensity of chemiluminescent radiation and the over-all rate of chemi-ion formation have been measured and the relative intensities of various individual chemi-ions have been observed with a T.O.F. mass spectrometer.

It has been shown conclusively from these measurements that chemi-ionization does not arise primarily from the reactions:



It has been shown also that if ionization arises from the reaction

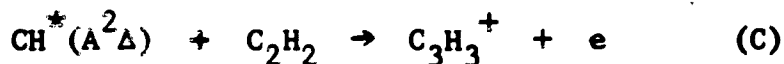
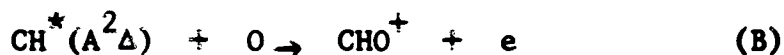
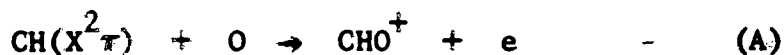


a mechanism that has also received wide support, then the ground state $\text{CH}(X^2\Sigma)$ molecule must be produced by some mechanism other than that producing $\text{CH}(A^2\Delta)$.

The $\text{CH } (A^2\Delta-X^2\Sigma)$ system was found to be the most intense feature of the chemiluminescent spectrum. Weak emission from the C_2 Swan bands and from the CN violet system was also observed. The intensity of the weak OH emission was found to be consistent with it being produced by reactions with molecular oxygen. The CH emission was shown to arise from a complex series of reactions involving the participation of 3 molecules of acetylene and 2 atoms of oxygen. Two possible mechanisms for its production are discussed.

INTRODUCTION

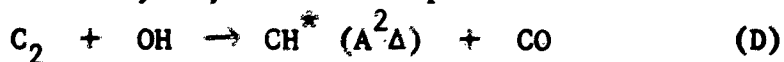
The room temperature reaction of atomic oxygen with acetylene exhibits intense chemi-ionization and chemiluminescence. The chemiluminescence spectrum has been described by Broida and Krishnamachari.¹ The most intense emission is produced by the $\text{CH}(A^2\Delta - X^2\Pi)$ system. Weaker emission from $\text{CH}(B^2\Sigma^- - X^2\Pi)$, C_2 , CN and OH are also observed. Chemi-ionization in this reaction was first observed by Fontijn and Baughman.² Later Fontijn, Hogan and Miller³ listed the most abundant ions in the system and noted the effect of carbon dioxide and several free radical scavengers on both the chemi-ion spectra and on the intensity of chemiluminescence. They proposed the following mechanism of chemi-ionization:



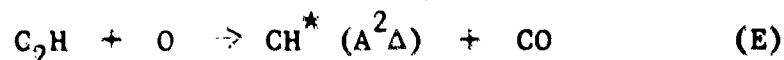
Reactions (B) and (C) were thought to be dominant.

Chemi-ionization in acetylene-oxygen systems has also received much study in flames^{4,5,6} and in shock waves.^{7,8,9} Much agreement exists as to the importance of reactions (A) and (B).^{4,5,6,7} Reaction (C) has also been postulated as a mechanism for the formation of the chemi-ion C_3H_3^+ ,^{5,8} which is the most important species in the high temperature oxidation of acetylene, although a recent paper by Kistiakowsky et al.⁹ has cast doubt upon this mechanism.

Less agreement exists as to the origin of chemiluminescence. Much of the work on acetylene-oxygen flames has been summarized by Gaydon.¹⁰ He prefers the reaction



to explain the production of excited CH species. However, the reaction



has received some support.^{7,9}

The present paper reports some results which pertain to the mechanism of chemi-ionization and chemiluminescence and which were obtained from a study of the reaction of atomic oxygen with acetylene in a moderately fast flow system. Chemi-ions were observed with a T.O.F. mass spectrometer. The rate of ion formation and the absolute intensity of chemiluminescent radiation were also measured.

EXPERIMENTAL

The reaction of oxygen atoms with acetylene was studied with apparatus and techniques very similar to those described in a previous paper.¹¹ The T.O.F. mass spectrometer was operated with ground potential on the backing grid. The electron beam could either be off or on depending on the purpose of the experiment. This allowed chemi-ions, formed in the reaction, to enter the spectrometer and be resolved independently or along with the charged species produced by electron beam ionization.⁹

The rate of ion formation was monitored by measurement of the current produced across two parallel platinum electrodes mounted in the flow reactor 1 cm. apart and operated at a potential difference sufficiently high to insure that all the ions produced between the plates were collected. The electrodes measured 1/2 cm. by 1/2 cm.; their position in the flow reactor was described in the previous paper.¹¹ In order to maintain a homogeneous electric

field between the electrodes, they were surrounded by guard rings. The guard rings also serve another purpose in that they make the measured rate of ion formation independent of the chemi-ion lifetime since they collect long lived ions from upstream and thus prevent them from reaching the main electrodes. Each guard ring consisted of a thin piece of platinum foil, 1 cm. by 1 cm., which was cemented onto a thin sheet of mica, 1/2 cm. by 1/2 cm., which had previously been cemented on to the back surface of each electrode. An electrical connection to the electrode was made through a small hole punched centrally in both the mica and platinum guard ring. The potential difference across the electrodes was supplied by a dry cell and a variable voltage divider. The current was measured with a Keithley Electrometer Model 600A.

In order to test the validity of the assumption that at sufficiently high potential difference all ions were collected by the electrodes, the current-voltage characteristics of the ionized gases produced in the reaction of atomic oxygen with acetylene were measured. With the electrodes 1 cm. apart and at a total pressure of 2.3 mm. Hg., a maximum current was measured at 40 V. potential difference. At potential differences greater than this the current remained at this maximum value. With the electrodes spaced 0.24 cm. apart the maximum current was reached at a potential difference of a little less than 10 V.

It has been shown recently¹² that vacuum ultra-violet chemiluminescence is produced in the reaction of atomic oxygen with acetylene. In order to insure that the photoelectric effect at the negative electrode was not contributing greatly to the total ionization, some experiments were performed with two electrodes which were widely different in size. One of these consisted of a thin platinum wire (0.005 inches in

diameter), all but the tip of which was shielded by pyrex tubing. The other electrode was a platinum sheet similar to that described above. The ion current with the small electrode positive was 8 times greater than that measured with the electrode polarities reversed. The ratio of the areas of the two electrodes was 5×10^{-4} . Thus we are confident that the photoelectric effect makes only a minor contribution to the total ionization, since the small difference in the measured ion currents can be well accounted for by the difference in the mobilities of the positively and negatively charged species.

The absolute intensity of chemiluminescent radiation emitted from the reaction was measured by comparison with that emitted from a tungsten lamp which had previously been calibrated at the National Bureau of Standards, Washington, D. C. The comparison was made with the apparatus described previously.¹¹

CHEMILUMINESCENCE

The main features of the chemiluminescent spectrum emitted in the reaction of oxygen atoms with acetylene are shown in Table 1. The spectrum is qualitatively similar to that obtained by Broida and Krishnamachari,¹ but the relative intensities of the various systems are somewhat different. In the present experiments the Swan bands of C_2 were not as prominent relative to the $CH(A^2\Delta - X^2\pi)$ system, and the CN bands were also less strong. However, the intensity of the CN system increased markedly in the presence of small amounts of untitrated atomic nitrogen. As reported by Broida et al.¹ addition of molecular oxygen decreased the intensity of the CH and C_2 bands and increased

the intensity of the OH system. The intensity of OH emission was measured to be proportional to the concentration of added molecular oxygen. In the absence of added oxygen the residual concentration of molecular oxygen, formed by recombination of oxygen atoms, was large enough to account for the observed intensity of OH chemiluminescence.

The absolute intensity of the light emitted by the $\text{CH}(\text{A}^2\Delta - \text{X}^2\Pi)$ system was measured by comparison with an NBS calibrated tungsten filament lamp. The results of two measurements are shown in Table 2. It can be seen by a comparison of the rate of photon emission and the total reaction rate that in these experiments one photon is emitted for every $10^3 - 10^4$ molecules of acetylene that are oxidized.

Fig. 1 shows the effect of the initial composition on the intensity of CH chemiluminescence emitted at a fixed reaction time. The intensity is plotted as a function of initial oxygen atom concentration, in Fig. 1 (a), on a log-log scale. In these acetylene rich mixtures the intensity is proportional to the square of the oxygen atom concentration. However, at small oxygen atom concentrations the over-all rate of reaction is directly proportional to the initial oxygen atom concentration.¹¹ Thus the ratio of the number of photons emitted to the number of oxygen atoms reacted increases with atomic oxygen concentration. It reaches a maximum in stoichiometric mixtures where the initial ratio of oxygen atoms to acetylene molecules is 2 : 1. Figure 1 (b) shows that the intensity of CH chemiluminescence is proportional to the cube of the acetylene concentration in oxygen rich mixtures.

As the reaction proceeds and reactants are consumed

the rate of photon emission decreases. Figure 2 shows both the acetylene concentration and the intensity of CH chemiluminescence as a function of the distance between the acetylene inlet and the point of observation. Since the linear flow velocity is constant, this distance is proportional to the reaction time before observation. The acetylene concentration was observed with a time-of-flight mass spectrometer and the intensity of chemiluminescence was measured with a 1P28 photomultiplier mounted so that light from a thin section across the reaction tube, perpendicular to the flow direction, passed through an interference filter and fell on the photomultiplier. The interference filter which isolated the $\text{CH}(\text{A}^2\Delta - \text{X}^2\Pi)$ system had a peak transmission at 4330 \AA and a band width of 60 \AA . The section from which emission was observed was 10 cm. upstream from the pinhole of the mass spectrometer; it was experimentally impossible to observe closer to the pinhole. In this experiment the initial concentration of atomic oxygen was three times as great as the initial acetylene concentration and the consumption of oxygen during the reaction produced only a 20 per cent decrease in the total atomic oxygen concentration. It can be seen that both the acetylene concentration and the intensity of chemiluminescence decay exponentially with time and that the exponential time constant for the decay of chemiluminescence is approximately three times greater than that for acetylene.

In an earlier paper¹¹ it was shown that acetylene is consumed in a bimolecular reaction with atomic oxygen:

$$\frac{d(\text{C}_2\text{H}_2)}{dt} = -k_1 (\text{O})(\text{C}_2\text{H}_2)$$

In the presence of a large steady excess concentration of atomic oxygen this expression integrates to:

$$\ln \frac{(C_2H_2)_o}{(C_2H_2)_t} = k_1 (O)_o t$$

where the subscript o refers to the initial concentration. Thus from Figure 2 it can be inferred that the intensity of CH radiation decays with time as the cube of the acetylene concentration. In a similar manner it was found that in acetylene rich mixtures the intensity of CH radiation decays with time as the square of the oxygen atom concentration. These results show a marked similarity to those derived from Figure 1, where the reaction time was held constant and the initial reactant concentrations were varied.

The rate of decay of chemiluminescence with reaction time was not changed by the addition of molecular oxygen although the absolute value of the intensity was decreased. In one experiment the decay of the weak chemiluminescence produced by C_2 was followed as a function of reaction time. In a mixture containing an excess of atomic oxygen the C_2 emission did not decay as fast as the CH radiation, but decayed as the square of the acetylene concentration. Thus the appearance of the flame changed from an intense blue to a faint green as one observed farther down the reaction tube at gases characteristic of longer reaction times.

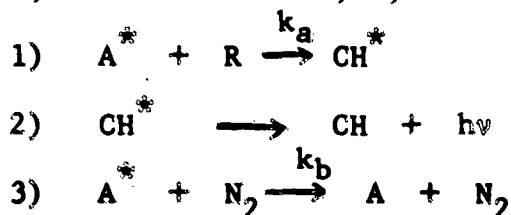
The effect of both pressure and temperature on the intensity of chemiluminescence are shown in Table 3. The intensity remained almost constant both when the pressure was increased tenfold and when the temperature was reduced from $300^\circ K$ to $195^\circ K$. The concentration of acetylene, recorded in Table 3, was estimated from measurements of the total pressure and of the flow rates of both nitrogen and acetylene. The concentration of atomic oxygen was estimated in a similar manner assuming one atom of oxygen to be formed for every

molecule of NO destroyed in the titration of atomic nitrogen. The relative concentration of atomic oxygen present in the experiments performed at 195°K and 300°K was estimated photometrically in a manner described previously.¹¹ Nitrogen and acetylene were assumed to obey the ideal gas laws.

It is clear from the results which have been presented above that the CH chemiluminescence is only a minor side product of the reaction of atomic oxygen with acetylene and that the participation of two oxygen atoms and three acetylene molecules are required to bring it about. The fact that the intensity of chemiluminescence is greatest in stoichiometric mixtures and decreases when either reactant is added in excess cannot be attributed to the effect of temperature since the intensity appears to be temperature independent, but must be due to competitive reactions of intermediates with various reaction partners. The reaction order must be interpreted in this sense. Chemiluminescence is obviously not fifth order in reactants since the intensity is a maximum in stoichiometric mixtures but the high order dependence on atomic oxygen and acetylene must arise from the fact that alternative reaction paths exist, only one of which leads to chemiluminescence. Each intermediate along this path must collide with a specific reaction partner for CH luminescence to be produced. Collision with other reactants leads to products other than CH ($A^2\Delta$).

It has been suggested that the main reaction proceeds via an addition reaction to form $C_2H_2O^*$ which decomposes unimolecularly to give triplet methylene radicals which are further oxidized to carbon monoxide and hydrogen probably via the intermediate HCO. The reactions which produce both methylene and HCO are very exothermic and either species could be produced initially in a state having energy well in

excess of that of the ground state. This excess energy could well be utilized if reaction takes place before the excited molecules are deactivated by collisions with nitrogen. If the reaction of one of these intermediates, A^* , produced at a rate Z , with a reactant, R , leads to chemiluminescence then:



Application of steady state treatment to A^* gives

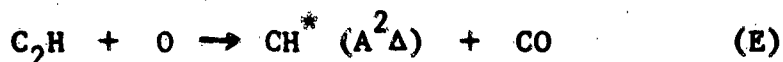
$$\text{Intensity} = \frac{d(h\nu)}{dt} = \frac{k_a(R) Z}{k_a(R) + k_b(N_2)}$$

Thus, the intensity of CH chemiluminescence depends upon (N_2) unless $k_a(R) \gg k_b(N_2)$. In these experiments we always have a hundredfold excess of nitrogen and thus in order for the above inequality to hold $k_a \gg 10^2 k_b$. The maximum value of k_a is that corresponding to reaction occurring at every collision between R and A^* , and even in this extreme case the inequality does not hold if A^* is normally deactivated by 100 collisions with N_2 .

Removal of excess rotational and translational energy almost certainly occurs within 100 collisions and the work of Herzberg et al.¹³ suggests that only 50 collisions with an inert gas remove most of the excess vibrational energy from singlet methylene radicals, produced in the photolysis of diazomethane. Larger hydrocarbon species are more efficiently deactivated from highly excited states¹⁴ and only simple diatomic species would be expected to survive more than 100 collisions before deactivation.¹⁵ Since the intensity of CH chemiluminescence was found to be almost independent of pressure (Table 3), it is likely that $CH(A^2\Delta)$ molecules are not produced by reactions of molecules having a large excess

of vibrational energy, unless these are simple diatomics.

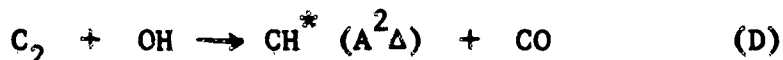
Also the mechanism leading to chemiluminescence cannot proceed via any reaction that requires an activation energy of more than about 1 kcal/mole, since neither the absolute chemiluminescent intensity nor the rate of the over-all reaction changed when the temperature was decreased from 300°K to 195°K. This latter requirement rules out the possibility of chemiluminescence arising from the reaction



in this system, since the reaction is endothermic by 5 kcal/mole.¹⁶ Also at least one of the reactions by which C_2H is thought to be produced, namely the abstraction reaction of oxygen atoms from acetylene, which is of importance at higher temperatures,⁹ is 14 kcal/mole endothermic:



The mechanism, D, proposed by Gaydon et al.¹⁰ looks, at first sight, very attractive



in light of the obvious complexity of reactions leading to chemiluminescence. This reaction received strong support from the work of Gaydon and Wolfhard¹⁷ who showed that when C_2H_2 was added to the discharge products of D_2O , [in which are produced mainly D, OD and O], the main chemiluminescence is emitted from the Swan bands of C_2 and from the CD ($\text{A}^2\Delta - \text{X}^2\Pi$) system. In flames of atomic oxygen the radiation from the Swan bands of C_2 is much less intense, however, and some doubt exists as to whether sufficient C_2 is produced to account for the observed intensity of CH chemiluminescence.

In our experiments the rate of photon emission from the CH ($\text{A}^2\Delta - \text{X}^2\Pi$) system was measured as 3×10^{13} photons/cc sec.

when $(O)_0 = 10^{15}$ molec/cc. and $(C_2H_2)_0 = 2.45 \times 10^{14}$ molec/cc. In this system (OH) cannot be more than a few per cent of (O) since the products of possible reactions of OH are only observed in very minor amounts.¹¹ Thus if one arbitrarily sets $(OH) = 3 \times 10^{13}$ molec/cc as an upper limit and assumes that reaction (D) occurs on every gas kinetic collision, then the concentration of C_2 necessary to produce the observed intensity of CH chemiluminescence is $\approx 10^{10}$ molec/cc. From the measured absolute intensity of CH chemiluminescence, the relative intensities of C_2 emission given in Table 1 and the mean lifetime of C_2^* ,¹⁸ one can calculate that $[C_2^*]$ is 2×10^5 molec/cc. Thus for reaction (D) to be responsible for CH chemiluminescence the population of the ground electronic states of C_2 would have to be $\sim 10^5$ that of the excited state. This corresponds to an electronic temperature of less than $2500^\circ K$, and thus it should be possible to show, by absorption measurements on the C_2 Swan bands, whether sufficient C_2 exists to make this mechanism possible. Gaydon et al.¹⁹ have made similar measurements in low pressure oxy-acetylene flames and have estimated the electronic temperature in these flames to be $3200^\circ K$. Unfortunately we do not have the necessary apparatus to perform such measurements on the C_2H_2/O system. However, for the stationary state concentration of C_2 to be as high as 10^{10} molec/cc.⁻¹, either C_2 must not be very reactive towards O, O_2 , H_2 , CO, and C_2H_2 , all of which are present in much larger concentrations than OH, or C_2 must be a very major reaction product. The latter is unlikely on energetic grounds and would contradict the findings of an earlier paper;¹¹ the former is improbable.

However, even if sufficient C_2 is present, other problems are presented by the acceptance of this mechanism. Recently Bayes and Jansson have shown that CH chemiluminescence

does not occur in acetylene systems in the absence of atomic oxygen.²⁰ If chemiluminescence does occur via reaction (D), it is not intuitively obvious why atomic oxygen is necessary, although it is possible that C_2 is formed only in the presence of oxygen atoms. Also, C_2 would have to be formed by a different mechanism to that producing C_2^* , since the rate of formation of C_2^* is at least an order of magnitude less than the rate of formation of $CH(A^2\Delta)$. Finally, one is left with the problem of postulating a mechanism capable of forming, in large quantities, a species having a heat of formation as large as that of C_2 .

To summarize, CH chemiluminescence is produced as a side product in the reaction of atomic oxygen with acetylene via a complex series of reactions which require the participation of two oxygen atoms and three acetylene molecules. The mechanism of chemiluminescence in this system evidently cannot involve reaction (E) and some doubt exists as to whether sufficient C_2 is formed for reaction (D) to be of major importance.

CHEMI-IONIZATION

The chemi-ion spectrum observed in the reaction of atomic oxygen with acetylene was very similar to that reported by Fontijn et al.³ However, the spectrum was extended to $m/e = 110$ and many high mass chemi-ions containing carbon and hydrogen were detected. Among the most abundant chemi-ions that were observed are CHO^+ , $C_2H_3O^+$, $C_3H_3^+$, $C_4H_5^+$, and H_3O^+ . The molecular formulas of these ions were assigned after making experiments with acetylene- d_2 . Under all of the conditions of the experiments the most abundant chemi-ion was $C_4H_5^+$. The relative abundance of all

of the ions varied with the initial composition of the reactants. In oxygen rich mixtures the ratio of the abundance of $C_3H_3^+$ to that of CHO^+ was proportional to the initial acetylene concentration.

An effort was made to identify the primary ion(s) by adding various substances to the system in an attempt to scavenge all secondary ions. Addition of H_2O in quantities comparable to the initial acetylene concentration led to an enhancement in the chemi-ion spectrum of high-mass ions containing H_2O and a depletion of most other ions. $C_4H_5^+$ was depleted by a factor of 10, while both CHO^+ and $C_3H_3^+$ were depleted by a factor of 4. Addition of NO to the reaction system led to the formation of large quantities of the ion NO^+ and a general nonpreferential depletion of all other chemi-ions.

The chemi-ion spectrum was also recorded in the reaction of methyl acetylene with atomic oxygen in an attempt to label one end of the acetylene molecule and thus to trace the pathway of reactions that lead to the formation of various prominent chemi-ions. This attempt proved unsuccessful since methyl acetylene reacts rapidly with oxygen atoms to form acetylene¹¹ and hence the chemi-ion spectrum was mainly that characteristic of the reaction of acetylene. However, a new ion CH_3CO^+ was more abundant than CHO^+ at least by a factor of 20 in an oxygen atom rich system.

The rate of formation of chemi-ions was calculated by measurement of the ion current across a pair of parallel plate electrodes operated at a sufficiently high potential to collect all of the chemi-ions formed between them. The rate of chemi-ion formation, R_f , varied as a function of the initial concentration of both acetylene and atomic oxygen as is

shown in Figure 3. It reached a maximum in stoichiometric mixtures. In acetylene rich mixtures the rate of ion formation is linearly dependent on the initial concentration of atomic oxygen, while in oxygen atom rich mixtures it is proportional to the initial acetylene concentration. Figure 3 (c) shows that the ratio of the rate of chemi-ion formation to the intensity of CH chemiluminescence varies as a function of mixture composition and that it is a maximum in a mixture in which the initial oxygen atom concentration is three times that of the initial acetylene concentration.

Under all of the conditions that were studied the rate of chemi-ion formation, R_f , decreased with increasing reaction time in a manner parallel to that of the CH chemiluminescence shown in Figure 2. Thus although the absolute rate of chemi-ion formation at any point in the reaction is proportional to the initial concentration of acetylene or atomic oxygen, the ion formation rate decreases throughout the reaction faster than either acetylene molecules or oxygen atoms are consumed. One possible explanation for this behavior is that ion formation is inhibited by the products of the reaction. In order to determine whether this was the case an experiment was performed in which a small quantity of acetylene was added to the atomic oxygen flow well upstream of the main acetylene inlet. Thus, the reaction at the main acetylene inlet was studied in the presence of the stable products of acetylene oxidation. It was found that the rate of chemi-ion formation was unchanged by the presence of these stable products and thus they must not inhibit ion formation. Therefore we must conclude that the concentration of one of the intermediates, whose reaction leads to chemi-ion formation, depends only linearly on the initial concentration of reactants but decays throughout the

reaction at a rate faster than that of the reactants. However we have been unable to detect such an intermediate with the mass spectrometer.

The relative concentrations of individual chemi-ions were measured throughout the reaction using the T.O.F. mass spectrometer and some of these observations are shown in Figure 4. The concentration of any individual chemi-ion depends both on the rate of ion formation and on the rate at which it is removed. Under the conditions of these experiments most of the negative charge is carried by ions²¹ and total charge is removed from the system by both ion-ion recombination and by ion recombination at the walls.³ However, it can be calculated that on the average each charge carrier makes about 10 - 100 gas kinetic collisions with either reactant before charge is lost by either of the two above-mentioned processes. Therefore most ions can be transformed by charge-transfer or ion-molecule reactions with neutral species. Since the rate of primary ion formation is known, from a measurement of the ion current across the platinum collector plates, the variation of the concentration of the primary ion(s) with reaction time can be computed if it is known by what mechanism the ion is removed. Thus it should be possible to compare this computed time-variation of the primary ion concentration with that experimentally determined for certain prominent chemi-ions and thus isolate which one is initially formed. Unfortunately, it would be mere speculation to go through this process at the present time since insufficient knowledge exists about the pathways of removal of $C_3H_3^+$, CHO^+ , $C_4H_5^+$, H_3O^+ , etc., but as the mechanisms of charge transfer reactions become clearer it should be possible to isolate the primary chemi-ion by this method using Figure 4.

The absolute rate of chemi-ion formation at an early stage of the reaction in two acetylene-atomic oxygen mixtures is shown in Table 2. Also shown are the results of simultaneous measurements of the absolute intensity of CH chemiluminescence and the rate of over-all reaction, which was calculated from the measured rate constant¹¹ and the ambient concentration of the reactants. If ions are formed by either reactions (B) or (C), then



where X is either acetylene or atomic oxygen. The rate of ion formation, R_f , is given by

$$R_f = \frac{d(\text{ions})}{dt} = k_1 (X) [\text{CH}(\text{A}^2\Delta)]$$

The radiative life-time, τ , of $\text{CH}(\text{A}^2\Delta)$ has been measured to be 5.6×10^{-7} sec,²² and $[\text{CH}(\text{A}^2\Delta)] = \tau I$, where I is the absolute intensity of CH chemiluminescence. If it is assumed that reactions (B) and (C) occur upon every gas kinetic collision, which is a reasonable upper limit since we are dealing with uncharged species, then the rate of ion formation from these reactions is:

$$R_f(\text{calc}) = 1.7 \times 10^{16} (X) I \text{ ions. cc.}^{-1} \text{sec.}^{-1} \quad (\text{F})$$

The value of $R_f(\text{calc})$ in Table 3 was determined from this equation using the ambient oxygen concentration in place of (X). It can be seen that this value is much less than the measured rate of ion formation and thus we must deduce that ions are mainly formed by reactions other than (B) and (C).

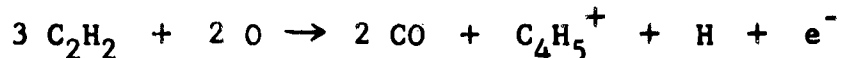
This conclusion is confirmed by the measurements shown in Figure 3 (c), where it is seen that the ratio of the ion formation rate to the intensity of chemiluminescence is more strongly dependent upon the initial composition than predicted by Eq. (F). It may be noted that the compositions

for which the absolute measurements of Table 2 were made are indicated in Figure 3 (c). An argument similar to that presented above also shows that ions cannot be formed in this system mainly by reactions of either C_2^* or OH^* .

It is clear from Figure 3 (c) and Table 2 that in order for reaction (A) to account for chemi-ion formation the population of the ground state of $CH(X^2\pi)$ would have to be much greater than that of the first excited state ($A^2\Delta$) and the relative population of these two states would have to be strongly dependent on the initial concentration of reactants. Recently Bleckrode and Nieuvoort have observed, for the first time, the $CH(A^2\Delta - X^2\pi)$ system in absorption in oxygen acetylene flames.²³ The absorption was extremely weak and no estimate of the absorption coefficient was given. Previously the $CH(C^2\Sigma - X^2\pi)$ system had been observed in absorption by both Gaydon et al.¹⁹ and by Norrish et al.²⁴ but the absorption was too weak to allow quantitative measurements to be made. Since the $CH(A^2\Delta - X^2\pi)$ transition is well allowed,²² the weakness of the absorption must indicate that the concentration of $CH(X^2\pi)$ is very low in these systems and thus some doubt must exist as to whether sufficient CH exists for reaction (A) to account for most of the chemi-ions formed.

The results of this investigation suggest that the formation of chemi-ions in this reaction is extremely complex and involves the participation of several acetylene molecules and oxygen atoms. Perhaps the reason for this complexity can be appreciated by realizing that the heat of formation of most organic chemi-ions is in excess of 200 kcal/mole. The interaction of several molecules of acetylene and oxygen atoms is required to produce this energy even if the other products of the reaction, CO, CO₂, and H₂O are of low

intrinsic energy. For example, one can write formally



which is thermoneutral only if $\Delta H_f(\text{C}_4\text{H}_5^+) = 280 \text{ kcal/mole}$.

Such a formal mechanistic description illustrates the large number of individual collision processes which may have to contribute in order to provide the energy required for ionization and also illustrates that in reactions of this complexity one cannot, a priori, ignore the possibility that even an ion as large as C_4H_5^+ may be the primary ion formed. In view of this it has proved impossible to find a unique mechanism which fits all of the experimental observations. However, it is clear that two mechanisms which are widely postulated as leading to chemi-ionization, namely mechanisms (A) and (B), cannot account for the chemi-ions formed in this system.

ACKNOWLEDGMENTS

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TABLE 1

RELATIVE INTENSITIES OF CHEMILUMINESCENCE FROM VARIOUS SYSTEMS

Species	Wave Length of Band-head (Å)	Relative Intensities [*] of Band-heads
$\text{CH}^* (\text{A}^2\Delta - \text{X}^2\pi)$	(0, 0)	1.00
	(1, 0)	0.007
C_2 (0, 0)	5165	0.04
C_2 (1, 0)	4737	0.017
C_2 (2, 1)	4715	0.015
C_2 (3, 2)	4697	0.011
C_2 (4, 3)	4684	0.006
C_2 (5, 4)	4678	0.001
$\text{OH} (\text{}^2\Sigma - \text{}^2\pi)$	3064	<0.0002
$\text{CH} (\text{B}^2\Sigma - \text{X}^2\pi)$	3871	0.016

* The measurements of relative intensity are given on a power basis, not on a quantum basis.

TABLE 2

THE ABSOLUTE INTENSITY OF CHEMILUMINESCENCE AND THE RATE
OF CHEMI-ION PRODUCTION

Mixture Composition (molec cc ⁻¹)	Over-all Reaction Rate (cc molec ⁻¹ sec ⁻¹)	Intensity of CH Chemiluminescence (photons cc ⁻¹ sec ⁻¹)	Rate of Ion Formation (ions cc ⁻¹ sec ⁻¹) (calc) (expt)
(a)			
(N ₂) = 6.1 x 10 ¹⁶	2 x 10 ¹⁶	3.42 x 10 ¹³	1.8 x 10 ¹² 7.5 x 10 ¹²
(O) _o = 9.8 x 10 ¹⁴			
(C ₂ H ₂) _o = 2.7 x 10 ¹⁴			
(b)			
(N ₂) = 8 x 10 ¹⁶	1 x 10 ¹⁶	1.52 x 10 ¹²	6 x 10 ¹⁰ 3 x 10 ¹²
(O) _o = 6.8 x 10 ¹⁴			
(C ₂ H ₂) _o = 1.7 x 10 ¹⁴			

TABLE 3

EFFECT OF PRESSURE AND TEMPERATURE ON CH CHEMILUMINESCENCE

Temperature (°K)	Mixture Composition (molec cc ⁻¹)			k_1 $\times 10^{14}$ (cc molec ⁻¹ sec ⁻¹)	Relative Intensity of CH*
	(N ₂) $\times 10^{-16}$	(O) $\times 10^{-14}$	(C ₂ H ₂) $\times 10^{-14}$		
293	5.1	6.1	1.2	10	1.00
195	7.6	4.0	1.7	9.0	0.91
293	24.0	4.7	1.0	9.0	1.00
293	2.7	4.7	1.0	7.1	1.6
293	6.9	10.0	1.0	6.6	0.33

* The relative intensities of the first two and the last three experiments were measured on different occasions and were only normalized with respect to themselves.

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FIGURE CAPTIONS

- FIG. 1** The effect of initial mixture composition on the intensity of CH chemiluminescence. Figure 1(a) shows the intensity plotted as a function of the initial oxygen concentration in a mixture rich in acetylene. $(N_2) = 6.9 \times 10^{16}$ molecules cc^{-1} , $(C_2H_2)_0 = 2.16 \times 10^{15}$ molecules cc^{-1} . Figure 1(b) shows the intensity as a function of acetylene concentration in a mixture having $(N_2) = 1.62 \times 10^{17}$ molecules cc^{-1} , $(O)_0 = 2.47 \times 10^{15}$ molecules cc^{-1} . Both plots are on a log-log scale.
- FIG. 2** The variation of the acetylene concentration and the intensity of CH chemiluminescence with reaction time. These measurements were made in a mixture rich in atomic oxygen. $(N_2) = 4.0 \times 10^{16}$ molecules cc^{-1} . $(O)_0 = 5.4 \times 10^{14}$ molecules cc^{-1} . $(O)_0 / (C_2H_2)_0 = 3.0$. Linear flow velocity = 566 cm. sec. $^{-1}$.
- FIG. 3** The effect of initial mixture composition on the rate of ion formation, R_f . In Fig. 3(a) the mixture is rich in atomic oxygen and $(O)_0 = 2.47 \times 10^{15}$ molecules cc^{-1} . In Fig. 3(b) the mixture is acetylene rich and $(C_2H_2) = 2.16 \times 10^{15}$ molecules cc^{-1} . The ratio of the intensity of CH chemiluminescence to the rate of ion formation is plotted in Fig. 3(c) as a function of the initial acetylene concentration for mixtures with $(O)_0 = 2.47 \times 10^{15}$ molecules cc^{-1} . The mixtures for which absolute intensity measurements were made are marked on this figure by Δ .
- FIG. 4** The relative concentrations of various chemi-ions are plotted as a function of the distance, down the flow tube, from the acetylene inlet. In Fig. 4(a), the mixture was rich in atomic oxygen. The dashed line

FIGURE CAPTIONS (Continued)

on this figure was drawn from a comparison with another experiment in which only the concentration of acetylene and the peak height of $m/e = 29$ were measured. Figure 4 (b) refers to a mixture rich in acetylene. The linear flow velocity in these experiments was approximately $700 \text{ cm. sec.}^{-1}$.

$M/e = 29$ is HCO^+ , $m/e = 39$ is C_3H_3^+ and $m/e = 53$ is C_4H_5^+ .

FIG. 1
LOG INTENSITY · ARBITRARY UNITS

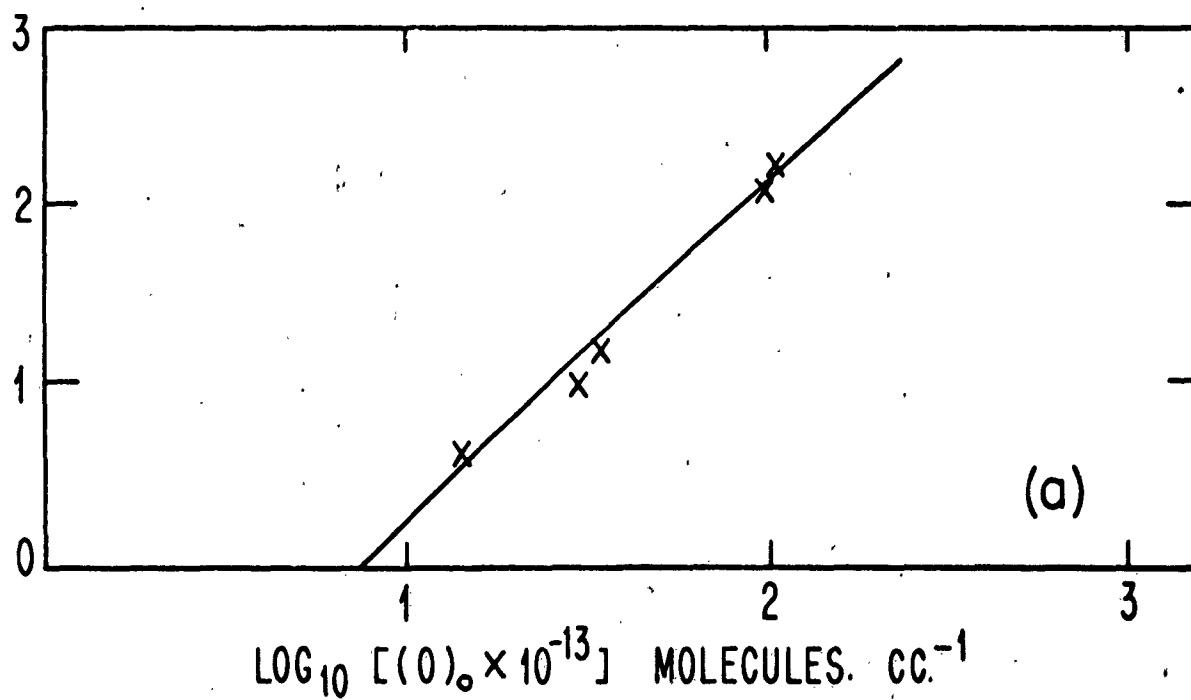
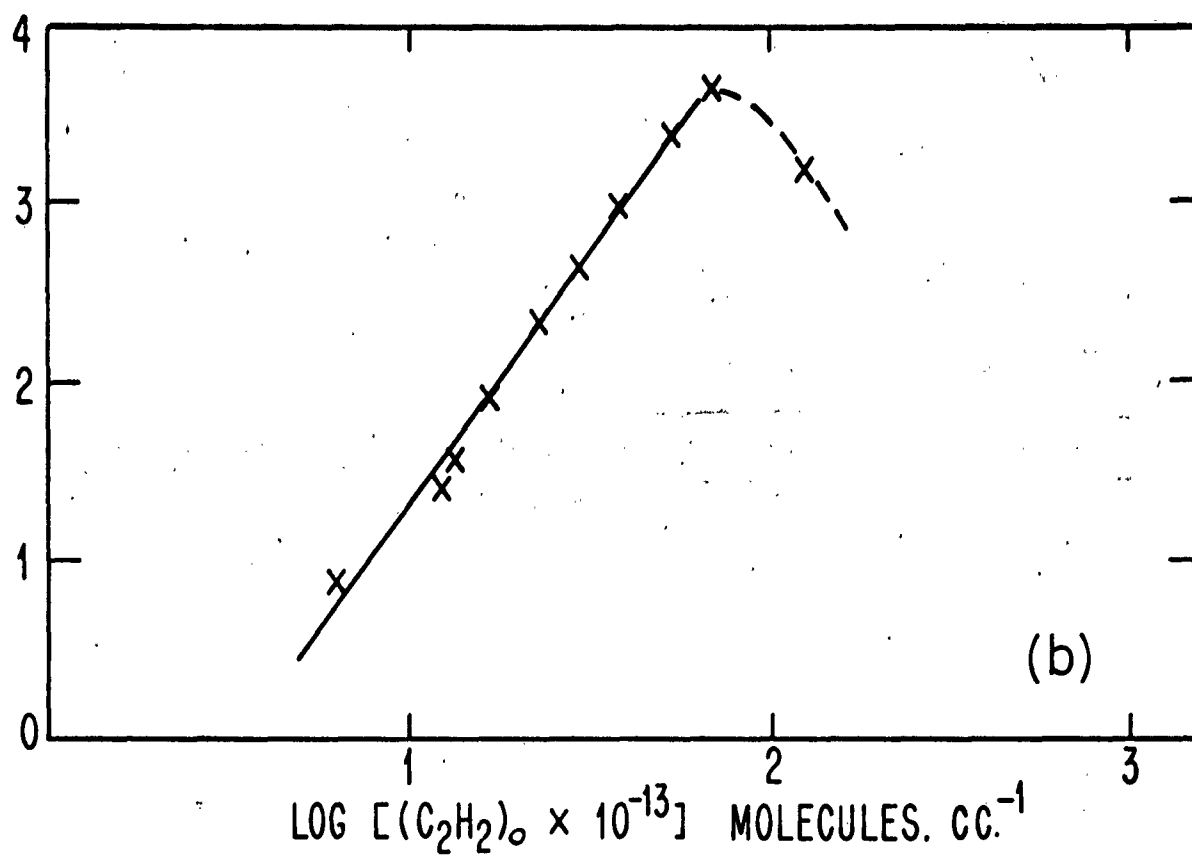


FIG. 2

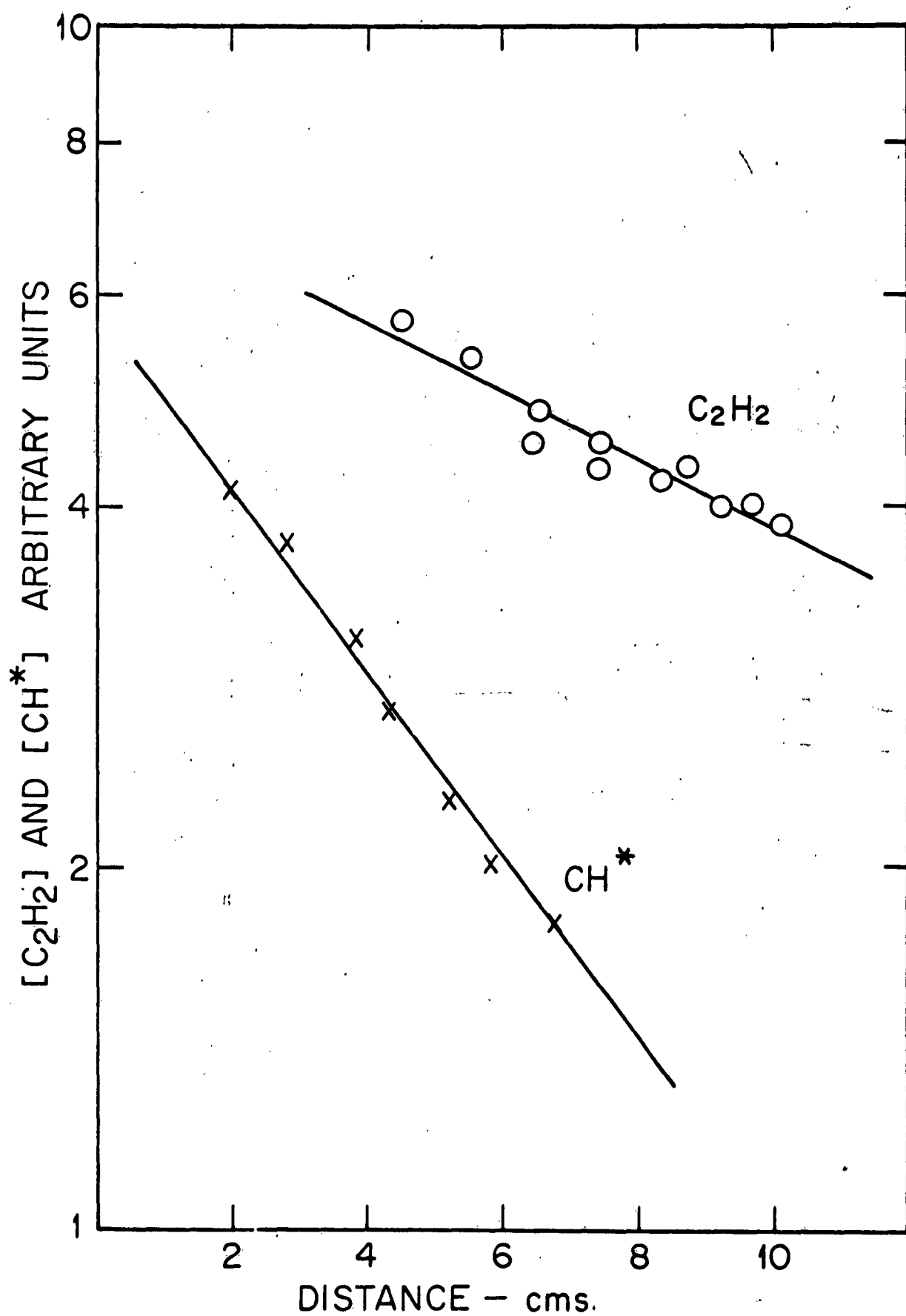


FIG. 3

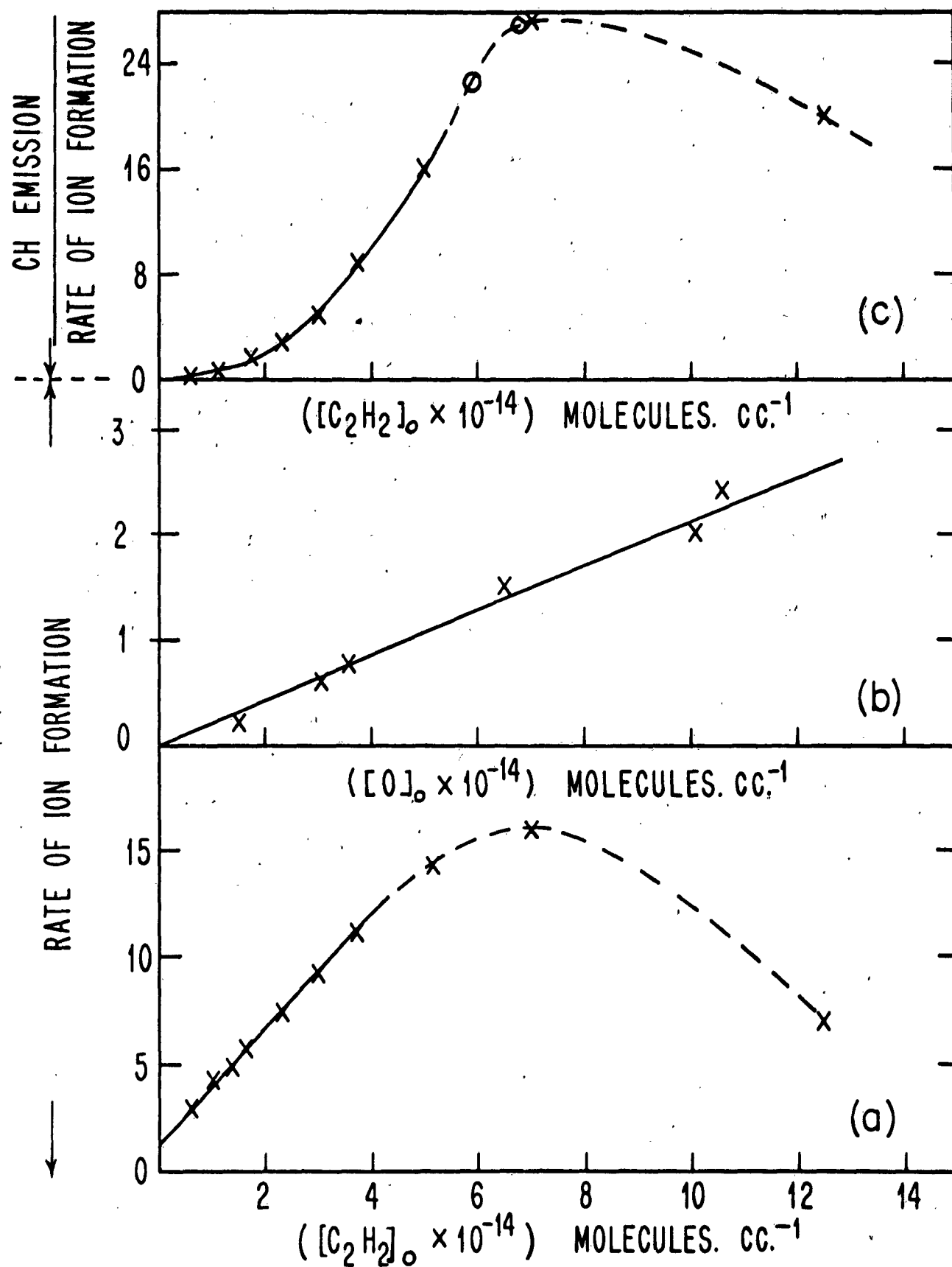


FIG. 4

CONCENTRATION OF VARIOUS CHEMI-IONS

